PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

On the Interpretation of the Indications of Atomic Structure Presented by Crystals when Interposed in the Path of X-Rays.

By William Barlow, F.R.S.

(Received June 22,—Read June 25,—Revised August 20, 1914.)

W. L. Bragg states in his exposition of the method of investigating the structure of crystals by means of X-rays, that a slight symmetrical distortion of the arrangement of the atoms, which would reduce the crystal symmetry, would not affect any of the results that he had just been describing.* Advancing considerably beyond this conclusion, it is proposed to show that a large amount of a certain kind of deformation of an atomic system arranged according to either of the three space-lattices possessing cubic symmetry, considerable enough to profoundly alter the nature of the arrangement, can take place without any appreciable evidence of this deformation being presented by the X-ray results. The argument consists of the proofs of the following propositions:—

Proposition 1.—Each of the three space-lattices which possess cubic symmetry can, by a simple modification, be converted into a regular point-system having this symmetry, but the system of trigonal axes of which, unlike that of the space-lattice, is of the non-intersecting kind.† The method employed to effect this modification is to so select one-fourth of the trigonal axes of the space-lattice concerned that no two of the selected axes

* 'Roy. Soc. Proc.,' A, vol. 89, p. 275.

† The system of non-intersecting axes of cubic symmetry is described by Barlow in Groth's 'Zeitschrift für Krystallographie,' vol. 23, p. 7 (figs. 1–3), also by Barlow and Pope, 'Trans. Chem. Soc.,' vol. 91, p. 1183.

intersect, and then to destroy the remaining three-fourths by symmetrically shifting each point of the space-lattice to the same extent in the appropriate direction along the selected trigonal axis on which it lies, and consequently away from the three other trigonal axes which passed through it. In the cases of the cubic space-lattice and the cube-centred space-lattice, the shifts can take place in both directions on an axis or in one only. The effect of any such symmetrical displacement of the points is that each of the selected axes continues to be a trigonal axis of the system of points, while each of the remaining three-fourths of the trigonal axes ceases to be so. The system of points resulting has cubic symmetry, but in nearly all the cases this is of a lower class than that of the space-lattice from which it is derived.

[*Added July* 20.—The following proof of this proposition is offered:—

Two of the three kinds of space-lattice referred to can each be regarded as consisting of interpenetrated component space-lattices of the remaining kind. Thus—(*a*) The points of the cubic space-lattice can be divided symmetrically into two identical sets in such a way that four of the eight points found at the corners of each cubic element are allotted to one set and the remaining four points to the other, each set of four thus allotted lying at the corners of a regular tetrahedron. The arrangement presented by half the points of the cubic space-lattice thus selected is easily seen to be that of the points of the face-centred lattice in which each point is equidistant from 12 nearest surrounding points. (*b*) The cube-centred space-lattice consists of two interpenetrating identical cubic space-lattices so related that the points of one of them lie at the centres of the cubic cells marked out by the points of the other. And since each cubic space-lattice is composed, as just pointed out, of two identical interpenetrated face-centred lattices, it follows that the cube-centred space-lattice consists of four symmetrically interpenetrated identical face-centred space-lattices. For the purposes of Proposition 1 the cubic space-lattice and the cube-centred space-lattice can therefore both be regarded as consisting of component face-centred space-lattices, and the proof of Proposition 1 for the latter which follows is easily extended to establish its validity for the other two space-lattices of the cubic system.

As to the application of Proposition 1 to the face-centred space-lattice:—

The system of non-intersecting trigonal axes of the cubic system can be generated from two non-intersecting axes the directions of which are inclined to one another at the angle subtended by two body diagonals of a cube. The process consists in continually locating additional axes of the same kind in such positions with respect to the two given axes and also to those from time to time added, that ultimately trigonal rotations through 120° made about any

one of the axes present become coincidence-movements of the unlimited system produced. The method is traced in detail in the journals just referred to.* The process indicated is available for the selection of one-fourth of the trigonal axes of the face-centred lattice required in Proposition 1 and when this selection has been made the coincidence-rotations proper to the system of non-intersecting trigonal axes thus located can be applied to the position after shift of a single point of the space-lattice in order to locate corresponding similar shifts of the remaining points consistent with the coincidence-movements in question. This is possible because the shifts take place along the selected trigonal axes; a condition which prevents the points of the point system generated by the coincidence-rotations from being more numerous than those of the space-lattice concerned. The direction of shift of one point of the face-centred lattice along its trigonal axis determines the direction of shift of every other point on its trigonal axis. The point-system generated from the single shifted point by carrying out the coincidence-rotations thus gives the result of making all the shifts prescribed in Proposition 1 symmetrically in harmony with the system of non-intersecting trigonal axes and presents the cubic symmetry proper to the system of rotations about these axes; the homogeneous structure obtained is that designated Type 1 in Barlow's list† and displays tetartohedral crystalline symmetry. The unaltered face-centred space-lattice is of type $8a_1$, which possesses holohedral crystalline symmetry.

As to the remaining two space-lattices of cubic symmetry:—

The method described of obtaining a regular point-system of cubic symmetry from a space-lattice can be applied to a cubic space-lattice in two different ways. For if, as above explained, we regard this lattice as composed of two interpenetrated face-centred lattices, the points of one component system found on a given trigonal axis may (1) move in the same direction as those of the other present on this axis, in which case, if the movements are equal, they will preserve an equal spacing on this axis, or (2) they may move in opposite directions, in which event equality of movement will result in higher crystal symmetry. Modification (1) of a cubic space-lattice, like that of a face-centred space-lattice above dealt with, produces a regular point-system of tetartohedral crystal symmetry; the type of homogeneous structure is No. 2 in Barlow's list. Modification (2), on the other hand, produces a regular point-system possessing pentagonal hemihedry; the homogeneous structure obtained is of type $1a_1$; the unaltered cubic space-lattice is of type $12a_1$.

* See note †, p. 1.

† 'Zeitschr. für Kryst.,' vol. 23, p. 7.

There are also two ways of applying the method to the cube-centred space-lattice. Thus—(a) the points of all four of the component face-centred lattices found lying on a given trigonal axis may be moved in the same direction on this axis; or (b) while the points of two of these component lattices, which together form a cubic space-lattice, found on a given axis are moved in the same direction, this direction may be opposite to that taken by the points of the remaining two found on the same axis. Modification (a) produces, in general, hemimorphic (tetrahedral) hemihedry of the cubic system; the type of homogeneous structure is then No. $2b_1$ in Barlow's list. It is an interesting fact, however, that a particular case of this modification yields holohedral symmetry. Thus, if the shifts of the points along their respective selected trigonal axes bring them to positions midway between the points of the unmodified cube-centred lattice, this highest crystal symmetry results. Modification (b) produces enantiomorphous hemihedry of the cubic system; the type of homogeneous structure is No. 3 or No. 4 in Barlow's list, according to the position of a shifted point on a trigonal axis with respect to the trigonal axes not parallel to this axis.

It is important to observe that additional diversity is achieved if the points of the two compound space-lattices are divided into their component face-centred lattices and the latter then subjected to different amounts of displacement. This inequality of shift of the points results in the production of an assemblage of points consisting of more than one Sohnckian regular point-system, but it is of interest to notice with regard to the cube-centred space-lattice that the shift of a point of one component cubic lattice can be so proportioned to that of a point of the other component cubic lattice lying on the same trigonal axis that the points of the cube-centred lattice become centres of symmetry of the system of shifted points. The two Sohnckian point-systems resulting are then so related as to form one double point-system, viz., a point-system the arrangement of half the points of which bears to that of the other half a mirror-image relation. In this event, instead of the tetartohedral symmetry of type 2, the pentagonal hemihedry of type $2a_1$ is presented. The unaltered cube-centred space-lattice is of type $13a_1$.

Plane diagrams of the above relations are not given here because the details are too involved for them to be useful. Models are needed for showing the three-dimensional properties referred to.

Proposition 2.—The method of modification defined in Proposition 1 makes the points of the space-lattice divisible into four sets, lying respectively on the four sets of differently orientated axes which constitute the selected system of non-intersecting trigonal axes. If, in addition to being equal, the displacements suffered by the points of such a set all have the same direction,

the planes of points found in this set will, it is evident, all present the same orientation and spacing before and after modification.

In the case of the face-centred lattice, the preservation of cubic symmetry requires that the displacements along an axis shall all be in the same direction, while for the other two kinds of space-lattice specified, opposite directions of shift are, as stated, possible for points of the lattice found on the same axis. In all but very exceptional cases, a system of parallel planes of points of one of the four sets just referred to is not congruent with the system of parallel planes having the same orientation of another set; in other words, in the entire system composed of the four sets adjoining spaces between successive parallel planes are neither equal nor present a simple rational relation.]

Proposition 3.—When the space-lattice concerned is regarded as consisting of parallel planes of points, the plane direction of which is perpendicular to one of its four sets of trigonal axes, each of these planes of points (111) is found to be broken up by the process of shifting prescribed into two distinct planes of points; one-fourth of the points of the original plane are shifted to a plane *a* parallel to it on one side, while the remaining three-fourths are shifted so as to be found in a plane *b*, also parallel to the original plane, but on the other side of it. The distance of the plane *a*, containing one-fourth of the points of the original selected plane, from that plane is three times that of the plane *b* containing the remaining three-fourths of the points.

The following proof is offered :—

Through opposite edges AB, CD (fig. 1, A and B), of one of the cubic elements of a cubic space-lattice draw a plane, and make this the plane of the diagram (B); this plane, besides the four points of the lattice A, B, C, D, contains, when produced, other points similarly situated at the corners of other cubic elements, as shown by the points of intersection of the horizontal and perpendicular lines of the figure.

Let AC be one of the surviving trigonal axes referred to in Proposition 1, and EAF the trace on the plane of the diagram of a plane perpendicular to AC drawn through A, which plane contains other points, such as E and F, of the space-lattice. One-fourth of the surviving trigonal axes, all of which intersect this plane, are perpendicular to it, and have the direction of AC; the remaining three-fourths, which have the other three directions for cube diagonals, all make the same angle with the same plane equal to the angle EAG, made by a diagonal of a cubic element of the space-lattice with the trace EAF.

Let P mark the point on the surviving trigonal axis AC to which the point A of the space-lattice is shifted: all points on trigonal axes parallel to AC originally found in the plane drawn through A perpendicular to AC will, after the shifting, lie in a plane parallel to this plane drawn through P.

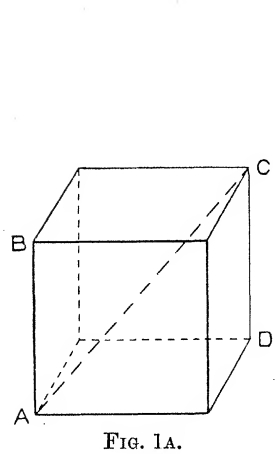

Fig. 1A.

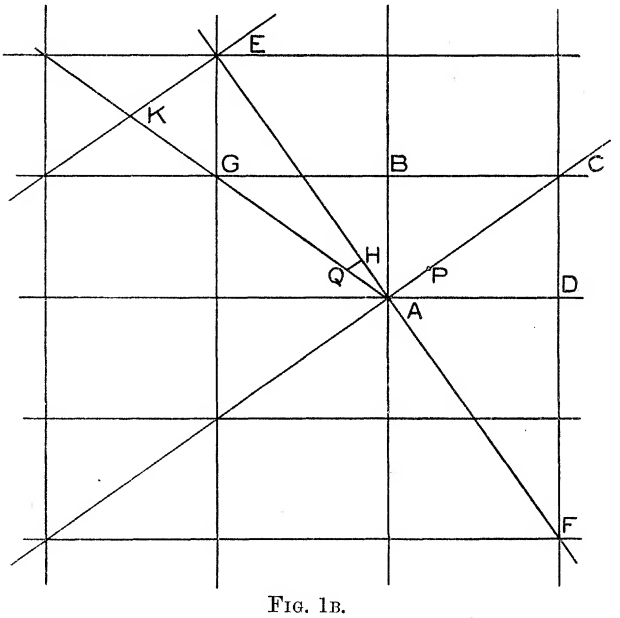

Fig. 1B.

Fig. 1.

The other points of the lattice contained in the plane EAF, which do not lie on the trigonal axes that have the direction AC, lie on trigonal axes having one or other of the three remaining directions for these axes, which directions all make angles equal to the angle EAG with this plane. And, as each of these points also experiences a shift equalling AP along its axis, they all lie in a plane parallel to the plane through EAF, passing through a point Q on the line AG, such that AQ = AP.

Draw QH, EK, both perpendicular to AE; EK is a semi-diagonal of a cubic element.

Since $\frac{QH}{AQ} = \frac{EK}{AK}$, and $3EK = AK$, it follows that $3QH = AQ = AP$.

Consequently, one-fourth of the points originally found in the plane having the trace EAF are shifted to a plane parallel to this plane, drawn through P at a distance = AP, while the remaining three-fourths are shifted in the opposite direction to a plane also parallel, drawn through point Q at a distance $HQ = AP/3$.

This proof is applicable to any plane (111) of points of either of the three space-lattices possessing cubic symmetry.

Proposition 4.—In the case of a regular system of similar atomic centres which is the outcome of a symmetrical displacement of the kind described, if the intensity of the portion of a given homogeneous (monochromatic) beam of X-rays thrown back at a given angle from a plane of the centres is taken to be proportional to the density with which the plane is beset with these centres, the intensities of two wave-trains travelling in the same direction, derived by similar reflection at the two planes (111) of atomic centres into which a single plane was resolved by the prescribed displacements, will, it is evident, be in the ratio 1 : 3, for plane *b* is three times as densely beset as plane *a*.

Proposition 5.—Since the displacement described converts a single plane (111) of atomic centres into two planes of centres, one of which is found on the one, the other on the other side of the original plane, it is evident that, of the two trains of reflected waves which thus take the place of a single train, one will present an advanced, the other a retarded phase, as compared with that of the single similarly reflected train which would be produced by the same beam falling on the unmodified plane of centres.

Proposition 6.—The phase presented by the resultant of the two wave-trains derived from the beam of X-rays, referred to in Proposition 4, is approximately the same as the phase of the wave-train which would be derived from the same beam by reflection at the unmodified plane of centres. Thus the phase of the resultant of the two reflected wave-trains is approximately constant for different values of the coefficient of displacement of the atomic centres. The following proof of this proposition is submitted :—

The geometrical convention adopted for the representation of waves of propagation of a ray of light consists of a sinuous line, the similar waves of which are of some given wave-length and express the amplitude of the

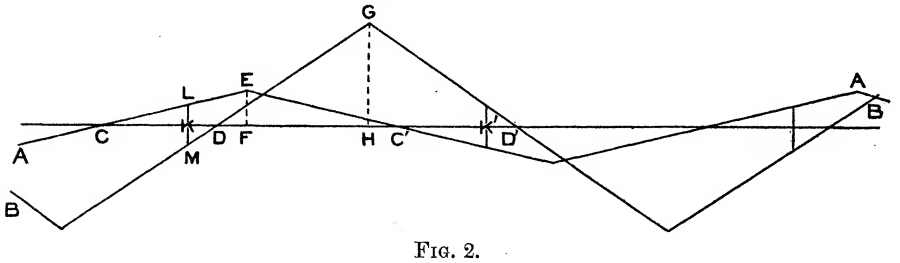

FIG. 2.

light waves by their transverse dimensions. In the case of the two reflected wave-trains referred to in Proposition 4, substitute zigzags for sinuous lines, and let zigzag A (fig. 2) represent the wave-train thrown back

from the plane which is less thickly beset with the atomic centres, zigzag B that reflected from the plane which is more so. If the maximum ordinate EF of A is p, GH, which is that of B, will then be $3p$.

The superposition of the two wave-trains is expressed by making their median lines coincide in the diagram. The difference in phase is given by the horizontal distance CD measured between nearest median points of the two wave-trains. The median points of the resultant wave-train, at which the ordinates of the component waves cancel each other as being of opposite sign and equal, are marked K, K′.

Since CF = DH, both being a quarter of a wave-length of the beam of X-rays, and 3EF = GH.

$$\text{Area } \Delta^e\text{DGH} = \frac{3\text{EF} \times \text{CF}}{2} = 3 \text{ area } \Delta^e\text{CEF},$$

Now $$\frac{\text{Area } \Delta^e\text{CLK}}{\text{Area } \Delta^e\text{CEF}} = \frac{\text{LK}^2}{\text{EF}^2}, \text{ and } \frac{\text{area } \Delta^e\text{DMK}}{\text{area } \Delta^e\text{DGH}} = \frac{\text{MK}^2}{\text{GH}^2} = \frac{\text{LK}^2}{9\,\text{EF}^2}.$$

Therefore $$\frac{\text{area } \Delta^e\text{CLK}}{\text{area } \Delta^e\text{DMK}} = \frac{\text{LK}^2 \times \text{area } \Delta^e\text{CEF} \times 9}{\text{LK}^2 \times \text{area } \Delta^e\text{DGH}} = \frac{9}{3} = 3.$$

But since LK = KM,

$$\frac{\text{Area } \Delta^e\text{CLK}}{\text{Area } \Delta^e\text{DMK}} = \frac{\text{CK}}{\text{KD}}; \quad \text{therefore} \quad \text{CK} = 3\,\text{KD}.$$

Now the difference in phase of the portion of a given wave-train reflected which would be produced by shifting the reflecting surface while maintaining its original plane direction is proportional to the amount of shift, *i.e.*, to the distance through which this surface is moved along a normal. Therefore if the difference in phase between the portion of the incident beam which would be reflected from the original plane and that reflected from a be m, the difference in phase between the former and that reflected from b will be $m/3$. Therefore, since CK = 3KD, the point K marks a median point of the wave-train reflected from the original plane of centres corresponding to the median points of the trains A and B marked respectively C and D. In other words the wave-train which is the resultant of these two wave-trains is in the same phase as the wave-train which would be produced by reflection of the given beam of X-rays at the unmodified plane. The similarity of the phases referred to would therefore be established not merely approximately but absolutely if the wave-trains were correctly represented by the zigzags of the diagram. If sinuous line waves are needed for the correct representation of the waves of X-rays concerned, and these line waves approximate more or less in form to the zigzags depicted, the relation deduced above will more or less approximately obtain, but not exactly.

Fig. 2 is drawn showing the difference of phase CD less than a quarter wave-length CF; the reasoning equally applies if it is shown greater.

Proposition 7.—A similar argument to that given above in respect of planes of centres (111), and found applicable to all the four sets of these planes, is available for the three sets of planes (100) and the six sets of planes (110). The reasoning employed for these will, however, be rather simpler than that given above in regard to planes (111), because the density of the distribution of the centres in the shifted planes is, for the plane directions (100) and (110) found to be equal in the two derived planes.

[*Added July* 20 : *Proposition* 8.—In all regular point-systems the arrangement of which is derived from one or other of the three space-lattices referred to by the method of modification described, every set of parallel equidistant planes of points presents an orientation and spacing of its consecutive planes strictly the same as those of the corresponding set of parallel planes of the lattice.

This is an immediate consequence of the equality of the shifts to which the points are subjected, and of these shifts forming sets, each of which has its own uniform direction.

Proposition 9.—The characteristic symmetrical distribution of X-ray intensity observed when homogeneous (monochromatic) X-rays are passed into a crystal of a simple compound belonging to the cubic system does not suffice to determine at all precisely the nature of the arrangement of the atoms. There is definite evidence of the existence of a precise dimensional relation between the wave-length of the X-rays employed and the actual magnitudes of the intervals separating successive planes of atomic centres in various directions, but this evidence does not suffice to show whether the atomic arrangement actually prevailing in the crystal is the space-lattice one compatible with the particular spacing of these planes indicated in the crystal under observation, or that of one of the innumerable various point-systems of cubic symmetry derivable from this space-lattice by the method described.

The following proof is submitted:—

The theory of the action of crystals on homogeneous (monochromatic) X-rays recently arrived at by W. H. Bragg and W. L. Bragg, suggested by their new experimental methods, may be shortly stated thus:—

1. The planes of atomic centres distinguishable in the regular systems according to which the homogeneous structures known as crystals are arranged, function as reflecting surfaces when impinged upon by a beam of X-rays.

2. Since every kind of plane of atomic centres present is repeated at uniform intervals so as to constitute a system of equidistant parallel planes, the phenomenon is over and over again presented of the beam falling on a series of parallel equally spaced reflecting surfaces, each of which acting alone can reflect but an imperceptible fraction of the incident radiation.

3. Reflection is thus more or less feeble unless the angle of incidence is such that the difference of phase of the portions of the beam reflected at the successive equidistant planes of such a series is congruent or very nearly congruent with the wave-length; in other words, unless the waves of the reflected wave-trains coincide and so reinforce one another. The familiar equation $n\lambda = 2d \sin \theta$ gives the glancing angles at which the intensity of the resultant reflected wave-train is a maximum; λ is the wave-length of the rays employed, θ the glancing angle of reflection, d the distance between the successive planes of the series of equidistant planes, and n a whole number. Thus reflection has maximum intensity at a series of angles θ_1, θ_2, θ_3, etc., the sines of which are in an arithmetical progression obtained by substituting integers 1, 2, 3, etc., for n.

The reader is reminded that any series of equidistant planes of atomic centres will commonly be intercalated with one or more similarly spaced series of planes of centres of the like orientation, the distance separating a plane of one series from a plane of another not, however, presenting a rational relation to the appropriate value of d.

4. A study of the comparative intensities of the first, second, third, and higher orders of spectra obtained from the variously orientated sets of planes leads to the discovery of the simplest scheme of atomic arrangement which would give comparative intensities for the different maxima in agreement with observation. The analysis is carried out by combining, mathematically, the waves of length λ reflected in the same direction from the various sets of planes, assigning to each wave an amplitude proportional to the mass per unit area of the plane which reflects it. By a process of trial and error an atomic arrangement is arrived at which would account for the observed intensities.

5. The various distances d for the differently orientated series of equidistant planes are calculated from the density of the crystal, the molecular weight of the unit of the crystal pattern and the comparative dimensions of the scheme of arrangement referred to in 4.

Now, as will have been seen from the foregoing, the regular point-systems derivable as explained fall into two classes, viz. :—

(a) Those in which the direction of displacement is the same for all points of the lattice found lying on the same trigonal axis.

(*b*) Those in which the points of the lattice found on a trigonal axis are some of them displaced in the one direction along this axis, the rest in the opposite direction.

All the cases of the modification of the face-centred space-lattice belong to class (*a*) (see p. 3).

Following the lines of this division into two classes a difference in the rigidity of the proof of Proposition 9 has to be noted. In cases of class (*a*) the proof is absolute; the difference in phase of the similar reflected wave-trains following a given direction produced by successive reflections at a number of parallel planes is precisely the same in the space-lattice arrangement as in any one of the point-system arrangements derived from this space-lattice by the defined method; and this is true whatever the direction chosen. This immediately follows from Proposition 8. For when the effect on the X-rays of a derived regular point-system is compared with that of the parent space-lattice and attention is confined to cases of class (*a*) it is clear that the break up of each plane of points of the space-lattice into two planes of points parallel to it (see Proposition 3) gives two component sets of reflected wave-trains in any given direction in place of each single set thrown back by the equally spaced parallel planes of a certain orientation of the space-lattice; and since each such component set presents the same phase difference as that characterising the corresponding set of the space-lattice, this phase difference will also be presented by the resultant set produced by the coalescence of the component sets referred to. Proposition 9 is therefore established for all cases of class (*a*), and it is clear that this conclusion is not affected by any question of the degree of accuracy attainable in the observations; the molecular weight of the unit of the crystal pattern is not affected by the modification contemplated, and although the number of distinct sets of parallel planes of centres is increased, the values d remain unchanged. However near precision the estimation of the results of the X-ray investigation may be, the argument based on them will therefore, in cases of class (*a*), fail to indicate which of the alternative atomic arrangements is the one actually prevailing; some additional fact is needed for determining this.

The proof of Proposition 9 for cases of class (*b*) rests on that of Proposition 6, which admittedly deals with approximations. This raises the question whether the quantitative results obtained experimentally are sufficiently precise to render even a very slight departure from the ideal distribution of intensity in the different directions adequate to rule out the solutions which involve this discrepancy. It is submitted that the degree of experimental refinement reached will not suffice for this. And, on the

other hand, very important considerations will be brought forward to show that in one particular instance a point-system arrangement, which differs profoundly from the space-lattice from which it is derived, manifests a much closer agreement with the experimental facts than this space-lattice does.

In comparing two kinds of atomic arrangement for the purpose of Proposition 9, the assemblages of atoms employed are taken to be similarly orientated; in other words they have corresponding axes parallel.

It follows directly from Propositions 6 and 8 that the phase-difference of successive reflected wave-trains following any given direction with respect to the axes is the same, within experimental error, for a space-lattice arrangement as for any point-system derived from this space-lattice by the method described. And the correspondence of the phase-differences for the same direction in two different arrangements carries with it similarity of the disposition of the directions of maximum intensity in any two assemblages related in the manner defined. Thus Proposition 9 is established to the degree of approximation afforded by Proposition 6. Additional data are therefore required for discovering the arrangement of the atoms in the molecule, and, indeed, for determining the nature of their distribution in space.

The particular case to which allusion has just been made will now be taken:—

W. L. Bragg has concluded* that the atoms of sodium and chlorine in the crystal of common salt NaCl very approximately occupy the points of a cubic space-lattice; the two component face-centred lattices of which the cubic lattice is made up (p. 2) mark respectively the suggested disposition of the two different kinds of atoms.

The need for some modification of this view is suggested by the fact that the arrangement reached does not lend itself to a distribution of the centres of the chemical molecules in harmony with the crystal symmetry. If the centres of the molecules NaCl are supposed to lie about half-way between nearest atom centres of the two kinds, the most symmetrical disposition possible for the molecular centres gives tetragonal symmetry; cubic symmetry is not attainable. Consequently, if molecules exist as individuals in the crystalline condition, such an arrangement must be out of harmony with the crystal form.

No such difficulty presents itself if the arrangement of the atoms is one derived from the cubic space-lattice by a certain application of the method of modification described. For let one-fourth of the trigonal axes of the cubic space-lattice be selected so as to furnish a cubic system of non-

* 'Roy. Soc. Proc.,' A, vol. 89, p. 469.

intersecting trigonal axes (p. 1): the two kinds of atoms are, according to Bragg's view, found placed alternately on each selected trigonal axis so that each atom lies midway, or about midway, between two atoms of the other kind present on the selected axis. Let, now, all the atoms of one kind present on one of the selected axes be moved uniformly towards one end of this axis, and all the atoms of the other kind found on this axis, to the same extent, towards the opposite end, neither kind of atom leaving the axis, and let the amount of displacement be such that the distance apart of the atoms of two kinds which have thus approached is slightly under the distance originally separating two nearest atoms. Let the atoms of two kinds which have approached be taken to form a molecule; all the molecules NaCl found on the axis taken are then similarly orientated. The carrying out of the coincidence-rotations about the axes of the system of non-intersecting trigonal axes will locate a similar atom arrangement on all the remaining trigonal axes and give an assemblage in accordance with the cubic symmetry of the system of axes. The centres of the molecules, if taken to lie midway between the centres of their atoms, are found arranged to form a face-centred lattice, although, in consequence of variety of orientation of the molecules, the assemblage does not present the high symmetry of this lattice.

A model of this scheme can be constructed to show both the symmetry of form of the polyhedral cell, which represents the domain of predominant influence of a single atom, and also the arrangement of the atoms and of the centres of the molecules. The following is the method of construction :—

Take a number of hollow indiarubber balls of the same size, and form pairs by sticking them together two and two; each pair is to represent a molecule. Arrange the points of contact, which are the centres of the pairs, to form a face-centred space-lattice, viz., as the sphere centres of a cubic closest-packed arrangement of equal spheres. Next, keeping the centres of the pairs in the relative situations prescribed, arrange the axes of the pairs symmetrically in four different orientations in harmony with the coincidence-movements of a set of non-intersecting trigonal axes. Finally, while preserving the relative arrangement of centres and axes thus reached, uniformly compress the mass so as to bring the pairs of balls together and flatten them at places of contact till all the interspaces are practically eliminated. In the resulting assemblage each ball centre is found nearly equidistant from 13 ball centres immediately surrounding it, and consequently each of the similar space-filling polyhedral cells producible by the process has 13 faces and is nearly capable of being circumscribed about a sphere. Thus the scheme reached immediately suggests stable equilibrium.

Since the atoms are of two kinds, but of the same fundamental valency, it is suggested that balls of two slightly different sizes may be used to represent the two kinds of atoms. The special relation of each atom to the one next to it with which it is chemically united to form a molecule suggests a shortening of the distance between each ball centre and the centre of the ball nearest to it on the same trigonal axis; the centre of the larger polyhedral face thus produced will practically coincide with the centre of the molecular group of two atoms.

It is clear from the foregoing that, while the scheme of arrangement suggested is in harmony with the X-ray results, it is in three respects in better agreement with the facts than the cubic space-lattice arrangement is. Thus: (1) The centres of the molecules are arranged according to cubic symmetry a condition impossible for the unaltered arrangement of the cubic space-lattice. (2) The symmetry indicated is not, like that of this lattice, holohedral, but is hemihedral, as are the actual crystals.* (3) Stable equilibrium is indicated by the relation of each centre to the centres immediately surrounding it.

In the model just described the distance apart of the centres of two balls representing the two atoms of the same molecule differs but little from that separating the centres of adjoining balls not thus related. It is, however, an interesting question whether the experimental facts are consistent with a much closer drawing together of the centres of the two related atoms, such that their distance apart becomes quite small compared with the distance separating nearest centres of the chemical molecules. The unit composed of two polyhedral cells, which represents the domain of predominant influence of a single molecule, would in such a case appear to approximate to sphericity and the enquiry arises whether this is possible without making the degree of approximation contemplated by Propositions 6 and 9 fall below the limit of experimental error of the X-ray methods.]

Proposition 10.—Inasmuch as every arrangement of points which displays cubic symmetry can be uniformly distorted to produce corresponding dispositions of the points exhibiting the kinds of symmetry of most of the other crystalline systems, and in this process the dimensional proportions in any given direction are preserved, it follows that, so far as geometrical possibilities are concerned, a very similar method of modification to that above described can be applied to all kinds of space-lattice arrangements of atoms of whatever symmetry, so as to produce from them point-systems

* The hemihedry of NaCl is not so clearly indicated as that of some of the allied halogen compounds KCl, KBr, etc., to which the arguments here given also apply.

which produce an effect on X-rays practically indistinguishable from that produced by the unmodified space-lattice arrangements respectively concerned.

It is therefore a general conclusion that the nature of the spacing of the parallel planes of atomic centres, as revealed by the results of the application of X-rays to crystals obtained by Laue and by W. H. Bragg and W. L. Bragg, is not so unambiguously indicated as at first appeared. For practical purposes these results are in many cases in harmony not only with the existence of very simple arrangements of the atoms according to an elementary space-lattice or combination of space-lattices, but are also equally consistent with a less symmetrical kind of arrangement derived by a considerable modification of the space-lattice or space-lattices, which leaves the system of crystal symmetry presented the same as before the alteration, but lowers the class. The fact that hemihedry is in so many cases presented by the crystals of simple compounds may be regarded as an indication that the actual arrangement of the atoms is of the less symmetrical kind.

But while insisting on the importance of ascertaining precisely the ambit of the new X-ray method of analysis of crystal structure, the author fully recognises that this method, as applied by W. H. Bragg and W. L. Bragg, is the basis on which the above conclusions rest; his argument, if sound, is an additional testimony to the value of this singularly beautiful form of research. And the admission that we are not so near to finality as at first appeared will make it more, not less, important to carry on the work. When in a given case the limits between which a solution must be sought have been found by the method, the student will doubtless be stimulated to examine the distinctive features of this case by all the means available, in order to find the additional factor needed for an exact determination.

A word in closing as to the bearing of the above conclusion on the work that has during the last few years been done in the investigation of atom arrangements from the standpoints of the chemist and crystallographer; this is largely based on observations of relative axial dimensions of crystals of allied substances, and on evidence as to the constancy of the proportionate volumes appropriated by the individual atoms, which is interpreted as indicating the existence of what is termed the law of valency volumes. In view of the above conclusions one is tempted to enquire whether it will not be possible in all cases to indicate an arrangement for the atoms of a crystal which is at the same time consistent with the results of an X-ray investigation and compatible with the conception that stable equilibrium is very approximately represented by a close packing of spheres of appropriate sizes, each of which stands for a single atom, variety of

pattern being attributed to modification of the spacing due to the presence of links which attach atom to atom to form certain groups or molecules and also to differences in magnitude of the atomic domains. A striking coincidence between chemical theory and a conclusion reached by means of the X-ray method of investigation gives pause, however. The arrangements which chemists assign in their graphic formulæ to the carbon atoms in the principal typical carbohydrates are precisely such as are presented by appropriate fractions of the point-system which Bragg has deduced as giving the arrangement of the carbon atoms in a crystal of diamond*; it is seen on examination that, so far as comparison is possible, precisely the same tetrahedral environment of each carbon atom is presented in both cases. Is it possible then that a tetrahedral group of four spheres in close contact forms a correct graphic representation of the four unit valency volumes of a carbon atom, and that a fitting of these tetrahedral groups closely together, which gives a distribution of their centres identical with that of Bragg's diamond structure,† correctly gives both the structure of this crystal and that of strings or chains of carbon atoms as they actually occur in the carbon compounds? The prospect seems inviting, but additional facts are needed to establish or modify such a conception, and to ascertain whether and how far it applies to other atoms than those which enter into the composition of organic compounds.

* 'Roy. Soc. Proc.,' A, vol. 89, p. 277.

† *Cf.* 'Scien. Proc. Roy. Dublin Soc.,' vol. 8, p. 542.